

GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION  
SPONSORED PROJECT INITIATION

Date: May 13, 1976

Project Title: Synthesis and Properties of Hydrocarbon Anions of Unusual Structure

Project No: G-33-614

Project Director: Dr. E. Grovenstein, Jr.

Sponsor: American Chemical Society

Agreement Period: From 9/1/76 Until 8/31/78

Type Agreement: Grant No. PRF 9127-AC4

Amount: \$24,000

Reports Required: As requested

Sponsor Contact Person (s):

Technical Matters

Contractual Matters  
(thru OCA)

Mr. Justin W. Collat  
Program Administrator  
Petroleum Research Fund  
American Chemical Society  
1155 Sixteenth Street, NW  
Washington, D. C. 20036

Defense Priority Rating:

Assigned to: Chemistry (School/Laboratory)

COPIES TO:

Project Director  
Division Chief (EES)  
School/Laboratory Director  
Dean/Director-EES  
Accounting Office  
Procurement Office  
Security Coordinator (OCA) ✓  
Reports Coordinator (OCA)

Library, Technical Reports Section  
Office of Computing Services  
Director, Physical Plant  
EES Information Office  
Project File (OCA)  
Project Code (GTRI)  
Other \_\_\_\_\_

GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION  
SPONSORED PROJECT TERMINATION

no action  
OK

Date: ~~12/11/78~~ 1/11/79 *CH*

Project Title: Synthesis and Properties of Hydrocarbon Anions of Unusual Structure

Project No: G-33-614

Project Director: Dr. E. Grovenstein, Jr.

Sponsor: American Chemical Society

Effective Termination Date: 8/31/78 (Grant Expiration)

Clearance of Accounting Charges: N/A - See ACS letter dated 8/23/78.

Grant/Contract Closeout Actions Remaining:

TERMINATED

- ☐ Final Invoice and Closing Documents
- ☒ Final Fiscal Report
- ☐ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other \_\_\_\_\_

Assigned to: Chemistry (School/Laboratory)

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Other \_\_\_\_\_

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and title pages important to the  
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RESEARCH PROGRESS REPORT

Page 1 of 1 pages.

Date Sept. 1, 1976 to Aug. 31, 1977

PRF# 9127-AC4

PRINCIPAL INVESTIGATOR(S)

Erling Grovenstein, Jr.

Please refer to instructions.

Fill in information requested above for each page.

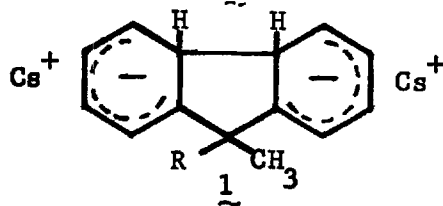
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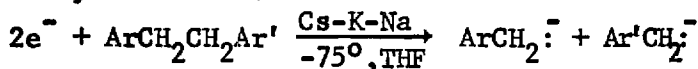
9127-AC4    Synthesis and Properties of  
Hydrocarbon Anions of Unusual Structure

Erling Grovenstein, Jr., Georgia Institute  
of Technology

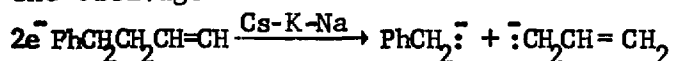
In contrast to 1,1,1-triphenylethane and 2,2-diphenylpropane which react with Cs-K-Na alloy in tetrahydrofuran (THF) at  $-75^{\circ}$  to give dianions 1 which are stable at



low temperatures (1,2), 1,2-diphenylethane, 1-phenyl-2-ortho-, meta-, and para-tolylethane, 1,2-di-m-tolylethane, 2,3-diphenylbutane, and 2,3-dimethyl-2,3-diphenylbutane are readily cleaved with excess of alloy to give an essentially quantitative yield of benzylic anions.



In like manner 4-phenyl-1-butene undergoes the cleavage



Competitive studies show that 2,3-dimethyl-2,3-diphenylbutane cleaves much more readily than 1,2-diphenylethane which cleaves slightly faster than 1-phenyl-2-m-tolylethane, 1,2-di-m-tolylethane, or 2,3-diphenylbutane; the latter cleave much more readily than 1-phenyl-2-p-tolylethane. These results may be interpreted in terms of facile cleavage of intermediate dianions (3).

- (1) Grovenstein, E., Jr., Beres, J. A., Cheng, Y.-M., Pegolotti, J. A., J. Org. Chem., (1972) 37, 1281.
- (2) Grovenstein, E., Jr., Longfield, T. H., Quest, D. E., J. Amer. Chem. Soc., (1977) 99, 2800.
- (3) Cf Lagendijk, A., Szwarc, M., J. Amer. Chem. Soc., (1971) 93, 5359.

PERSONNEL STATEMENT

PRF# 9127-AC4 REPORTING PERIOD Sept. 1, 1976 TO Aug. 31, 1977  
 GRANTEE INSTITUTION Georgia Institute of Technology DEPARTMENT School of Chemistry  
 PRINCIPAL INVESTIGATOR(S) Erling Grovenstein, Jr.  
 GRANT PROJECT TITLE Synthesis and Properties of Hydrocarbon Anions of Unusual Structure

List undergraduate, graduate, and postdoctoral co-workers receiving stipends under the above named grant:

NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION & DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
Dr. Dibyendu Sengupta	Postdoctorate	Ph. D. Univ. Lucknow	India	11.5	100	None

List other co-workers on grant project not directly supported with ACS - PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT
Dean E. Quest	NSF	Preliminary experiments, Summer and Fall, 1977

\* For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph. D. granting institution.

GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

OFFICE OF  
THE DIRECTOR OF  
FINANCIAL AFFAIRS

October 4, 1977

The Petroleum Research Fund  
Americal Chemical Society  
1155 Sixteenth Street, N.W.  
Washington, D. C. 20036

Gentlemen:

Enclosed in duplicate is the Annual Financial Statement for PRF No. 9127-AC4 covering the period September 1, 1976 through August 31, 1977.

If you have questions or desire any additional information, please let us know.

Sincerely yours,

Evan Crosby  
Associate Director of  
Financial Affairs

EC/bs

Enclosures: as stated  
cc: Dr. E. Grovenstein, Jr.  
Dr. J. A. Bertrand  
Mr. E. E. Renfro  
Mr. A. H. Becker  
File G-33-614

ANNUAL FINANCIAL STATEMENT  
(Insert "Annual" or "Final", as appropriate)

AMERICAN CHEMICAL SOCIETY - THE PETROLEUM RESEARCH FUND

For the Period: 9/1/76 to 8/31/77  
(August 31 is the preferred closing date for the reporting period)

Balance at Start of Reporting Period	.00
Received from PRF During Reporting Period	<u>\$ 12,000.00</u>
Salaries to:	
Principal Investigator	.00
(Contribution toward summer salary*)	
Graduate or Undergraduate Students	.00
Postdoctoral Fellows	<u>\$ 9,104.09</u>
	.00
Fellowships or Scholarships to:	
Undergraduate Scholars	.00
Graduate Fellows	.00
Postdoctoral Fellows	.00
Tuition	.00
Materials and Supplies	<u>1,139.46</u>
Equipment	.00
Travel	.00
Other Expenses	.00
Institutional Supplement*	<u>155.00</u>
Departmental Supplement or Allocation*	<u>500.00</u>
* If provided in grant agreement	
	<u>\$ 10,898.55</u>
Total Expenditures During Reporting Period	
Balance on Hand at End of Period	<u>1,101.45</u>
Total of PRF Grant Payments Received to Date	<u>\$ 12,000.00</u>

Complete this section only for a FINAL FINANCIAL STATEMENT which shows a balance in the grant account.

The balance in the grant account will be liquidated

☐ By refund of unspent and uncommitted funds. The check should be drawn to the order of American Chemical Society - The Petroleum Research Fund, and identified by the number of the grant.

☐ By use in the completion of the grant project. We hereby request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds until \_\_\_\_\_, (period up to one year, renewable).

We certify that the expenses reported herein were incurred for education and research in accord with the terms of the approved ACS-PRF grant-in-aid.

Georgia Institute of Technology  
(Grantee Institution)

By Evan Crosby, Associate  
Financial Officer/Director of Financial Affairs

Dr. F. Grovenstein, Jr.  
(Name of Principal Investigator)

10/4/77  
(Date)

9127-AC4  
(PRF No.)

Q33-64  
19

GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

CHEMISTRY

September 26, 1978

Dr. Justin W. Collat  
Program Administrator  
Petroleum Research Fund  
1155 Sixteenth Street, N. W.  
Washington, D. C. 20036

Dear Justin:

You will find enclosed our Final Annual Report of Progress and Personnel Statement for PRF Grant No. 9127-AC4. Our Business and Finance Office will send you by separate mail our Final Financial Statement. Dr. Sengupta is presently checking and refining some of his data; we hope to be able to submit the major portion of his work for publication within three or four months.

The support which the Petroleum Research Fund has given our work is greatly appreciated.

Sincerely,

Erling Grovenstein, Jr.  
Brown Professor of Chemistry

EG/mw

Encls.

CC:

(2 copies sent to PRF)

## RESEARCH PROGRESS REPORT

Page 1 of 2 pages.Date September 26, 1978PRF# 9127-AC4

## PRINCIPAL INVESTIGATOR(S)

Erling Grovenstein, Jr.

Please refer to instructions.

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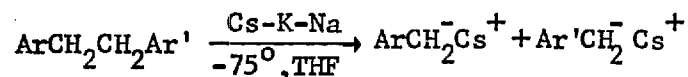
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## 9127-AC4 Synthesis and Properties of Hydrocarbon Anions of Unusual Structure

Erling Grovenstein, Jr., Georgia Institute of Technology

In contrast to 1,1,1-triphenylethane and 2,2-diphenylpropane which react with Cs-K-Na alloy in tetrahydrofuran (THF) at  $-75^{\circ}$  to give dianions which are stable at low temperatures<sup>1,2</sup>, 1,2-diphenylethane and eleven of its methylated derivatives are cleaved with excess of alloy in quantitative yield to benzylic anions.



Studies in which Cs-K-Na alloy was allowed to react competitively with an excess of two hydrocarbons gave the following relative rates of cleavage: 2,3-dimethyl-2,3-diphenylbutane, 21; 1-(2,6-dimethylphenyl)-2-phenylethane, 4.3; 1-phenyl-2-*o*-tolylethane, 1.9; 1,2-bis(*o*-tolyl)ethane, 2.1; 1,2-diphenylethane, 1.00; 1-phenyl-2-*m*-tolylethane, 0.51; 1,2-bis(*m*-tolyl)ethane, 0.34; *meso*-2,3-diphenylbutane, 0.30; 1-(3,5-dimethylphenyl)-2-phenylethane, 0.27; 1,2-bis(3,5-dimethylphenyl)ethane, 0.077; 1-phenyl-2-*p*-tolylethane, 0.025; and 1,2-bis(2,6-dimethylphenyl)ethane, 0.024.

A Hammett plot of the logarithm of these relative rates of cleavage versus  $\Sigma \sigma$ , where  $\sigma_m$  and  $\sigma_p$  are taken from the equilibrium acidities of *m*- and *p*-xylene relative to toluene<sup>3</sup> is linear for the *meta* and *para* derivatives of diphenylethane. Hence these results may be interpreted in terms of cleavage of intermediate dianions, as ion pairs, according to a mechanism similar to that proposed by Lagendijk and Szwarc<sup>4</sup> for cleavage of 1,2-bis( $\alpha$ -naphthyl)ethane. Evidently intimate ion pairs are normally involved since the relative rate of cleavage of 1-phenyl-2-*p*-tolylethane is greatly increased by addition of 18-crown-6.



RESEARCH PROGRESS REPORT

Page 2 of 2 pages.

Date September 26, 1978

PRF# 9127-AC4

PRINCIPAL INVESTIGATOR(S)

Erling Grovenstein, Jr.

- (1) Grovenstein, E., Jr., Beres, J. A.,  
Cheng, Y.-M., Pegolotti, J. A.,  
J. Org. Chem., (1972) 37, 1281.
- (2) Grovenstein, E., Jr., Longfield, T. H.,  
Quest, D. E., J. Am. Chem. Soc.,  
(1977) 99, 2800.
- (3) Gay, G., Marque, S., J. Am. Chem. Soc.,  
(1976) 98, 1538.
- (4) Lagendijk, A., Szwarc, M., J. Am.  
Chem. Soc., (1971) 93, 5359.

Please refer to instructions.

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PERSONNEL STATEMENT

PRF# 9127-AC4 REPORTING PERIOD September 1, 1977 TO September 15, 1978

GRANTEE INSTITUTION Georgia Institute of Technology DEPARTMENT Chemistry

PRINCIPAL INVESTIGATOR(S) Erling Grovenstein, Jr.

GRANT PROJECT TITLE Synthesis and Properties of Hydrocarbon Anions of Unusual Structure

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NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION & DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
Dr. Dibyendu Sengupta	Postdoctoral Associate	Ph.D., Univ. of Lucknow, India	India	12½	100%	-

List other co-workers on grant project not directly supported with ACS - PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT

\* For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph. D. granting institution.